DIETARY INTAKE OF POLYBROMINATED DIPHENYL ETHERS (PBDES) AND HEXA-BROMINATED BIPHENYLS (HEXA-BBS) FROM FRESH FOODS AROUND TAIWAN

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Introduction

The environmental hormones, polybrominated diphenyl ethers (PBDEs) and hexa-brominated biphenyls (Hexa-BBs), are persistent, difficult to decompose biologically but easy to accumulative in the environment. Tetra-BDEs, Penta-BDEs, Hexa-BDEs, Hepta-BDEs, Octa-BDEs, and Hexa-BBs are listed in the Stockholm Convention on the persistent organic pollutants. PBDEs and Hexa-BBs are the commonly used brominated flame retardants (BFRs) in industrial world, added in daily necessities, electronic products and building materials as flame retardants to delay or suppress fires. Hexa-BBs were produced until 1980s and the production of PBDEs was prohibited gradually in 2006. Restriction of The Use of Certain Hazardous Substance in EEE (RoHS) stipulates that Member States shall ensure that, from July 2006, new electrical and electronic equipment put on the market does not contain PBDEs and Hexa-BBs. Because PBDEs and Hexa-BBs will bio-accumulate through the food chain, and the long-term intake and accumulation will disrupt the organism's endocrine system, and even cause neurobehavioral deficits, reproductive toxicity and possibly cause cancer in laboratory animals[1]. Therefore, it is urgent and necessary to establish the completed analyzed technology and continuously long-term monitoring to determine whether domestic commercial food is contaminated or not. The objectives of this study were to identify possible local sources of contamination. Moreover, we used a TDS approach to compare the dietary exposures to PBDEs and Hexa-BBs with the MOE and NOEL by European Food Safety Authority (EFSA), respectively.

Materials and methods

The systematic sampling method was used to collect a wide variety of foods in fifteen categories of 600 food samples. We first selected the township with highest food production as the sampling locations according to the statistics from the Council of Agriculture and Fisheries Department. Second, different foodstuff samples were purchased from traditional markets or supermarkets in selected towns around Taiwan from 2010 to 2013. Finally, we used over 600 individual foods in the four years to prepare samples. All samples were adequately homogenized, and then frozen at −20°C until analysis. For example, a pork composite sample weighing 600 g was prepared by homogenizing 10 aliquots of 60 g of homogenized pork, each from separate pork samples of ca. 500-1000 g. We used isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) to measure 24 PBDEs and 5 Hexa-BBs congeners in livestock, poultry, fish, seafood, eggs, milk, dairy products, and oil samples, as previously described[2]. Analytical procedures were adopted from USEPA Method 1614A with minor modifications. The total PBDE concentration was calculated by summing all the concentrations of the 24 individual congeners measured. We estimated the daily intake (EDI) of PBDEs based on the ingestion rate of foodstuffs by a gender- and age-specified population database derived from the Nutrition and Health Surveys in Taiwan (NAHSIT) conducted in 2001-2002 and 2005-2008, and from the measured concentrations of PBDEs and Hexa-BBs in the corresponding food item from our laboratory. The distributions of EDI values were analyzed using Monte Carlo simulation techniques to obtain probabilistic parameters such as percentile values. In the absence of a TDI for PBDEs, a MOE approach was used to determine the health risk of dietary PBDE exposure of the population. EFSA identified the effects on neurodevelopment as the critical endpoint, and derived the reference dose for BDE-47 is 172 ng/kg bw/day, for BDE-99 is 4.2 ng/kg bw/day, for BDE-153 is 9.6 ng/kg bw/day, and BDE-209 is 1.7 mg/kg bw/day. The MOE can be calculated by comparing the reference dose with the Monte Carlo estimated 95th percentile dietary exposure (MCS P95) of the population. EFSA considered that an MOE larger than 2.5 might indicate that there is no health concern[3]. In addition, the EFSA Panel on Contaminants in the Food Chain (CONTAM

Panel) selected the hepatic carcinogenic effects as the critical effect of Hexa-BBs, with a no observed-effect level (NOEL) of 0.15 mg/kg body weight[4].

Results and discussion

Based on per gram fresh weight, the highest PBDEs level was found in oils (mean= 1418 pg/g fresh weight), followed by eggs (mean= 960 pg/g fresh weight), livestock (mean= 950 pg/g fresh weight), giblets (mean= 825 pg/g fresh weight) and fish (mean= 716 pg/g fresh weight), and lowest for mushrooms (mean= 122 pg/g fresh weight) (Table 1). The highest Hexa-BBs level was found in fish (mean= 2.48 pg/g fresh weight), followed by eggs (mean= 1.32 pg/g fresh weight), livestock (mean= 1.14 pg/g fresh weight), poultry (mean= 0.990 pg/g fresh weight), other seafood (mean= 0.457 pg/g fresh weight), infant foods (mean= 0.200 pg/g fresh weight), and lowest for dairy products (mean= 0.159 pg/g fresh weight). The high PBDE level in "oils" was contributed by the Canola oil that were found to contain the highest PBDE level (mean= 3831 pg/g fresh weight) among all food items. After integrating four background surveys of PBDEs levels from 2010 to 2013, the highest of estimated daily intake (EDI) of PBDEs from Taiwanese food consumption was found in 0-3 years old group (9.38 ng/kg/day, the 95% upper limit of Monte Carlo Simulation (MCS P95) was 21.52 ng/kg/day), and lowest in 17-18 years old female (3.35 ng/kg/day, the MCS P95 was 6.53 ng/kg/day) (Table 2). The EDI of PBDEs in all age groups of this study are lower than the JECFA's reference dose 100 μg/kg/day, which was used to evaluate the health risk of PBDEs by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 2005[5]. According the analyzed data from this study, the highest of EDI of Hexa-BBs from Taiwanese food consumption was found in 0-3 years old (0.007 ng/kg/day, the MCS P95 was 0.019 ng/kg/day), and lowest in 17-18 years old female (0.002 ng/kg/day, the MCS P95 was 0.005 ng/kg/day). The EDI of Hexa-BBs in all age groups of this study are lower than the EFSA's reference dose 0.15 mg/kg/day, which was the used to evaluate health risk of PBBs by EFSA Panel on Contaminants in the Food Chain in 2011. The results show that all the MOEs for the four congeners were greater than 2.5.

However, the MOE of BDE-99 for all age groups, MOE of BDE-153 for younger groups (under age 16) are still less than 100, which raise a point of concern that health effect caused by BDE-99 and BDE-153. This study suggests that the large MOEs (>2.5) calculated following EFSA's approach for the four important congeners BDE-47, BDE-99, BDE-153 and BDE-209 indicate that the estimated dietary exposures are unlikely to be a significant health concern for Taiwanese.

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Reference

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Table 1 PBDEs and Hexa-BBs contents in diet samples (pg/g fresh weight)

Food	N	ΣPBDEs	N	ΣHxBBs
Rice	**6**	**354 (123-952)**	-	-
Crain Crops	**12**	**269 (34.1-1433)**	-	-
Beans	**12**	**385 (72.5-853)**	-	-
Vegetables	**36**	**123 (12.1-1193)**	-	-
Mushrooms	**12**	**122(25.6-280)**	-	-
Poultry	**78**	**648 (99.0-3098)**	**30**	**0.990 (0.123-16.0)**
Chicken	26	507 (107-1520)	10	0.200 (0.123-0.347)
Duck	26	617 (99.0-1465)	10	1.85 (0.141-16.0)
Goose	26	820 (252-3098)	10	0.921 (0.318-4.95)
Livestock	**84**	**950 (66.4-10799)**	**30**	**1.14 (0.092-7.18)**
Pork	28	1003 (219-3359)	10	0.551 (0.092-2.44)
Beef	24	701 (66.4-3105)	6	1.28 (0.160-2.41)
Mutton	24	1381 (74.0-10799)	6	2.48 (0.271-7.18)
Imported Beef	4	192 (104-352)	4	1.12 (0.112-4.01)
Imported Mutton	4	240 (190-279)	4	0.438 (0.225-0.934)
Giblets	**18**	825 (119-1830)	-	-
Haslet	**12**	439 (76.1-1848)	-	-
Eggs	**46**	**960 (174-4345)**	**10**	**1.32 (0.267-5.31)**
Chicken Eggs	23	739 (174-1741)	5	0.982 (0.267-2.69)
Duck Eggs	23	1180 (347-4345)	5	1.66 (0.423-5.31)
Oils	**36**	**1418 (249-8868)**	-	-
Fish	**92**	**716 (97.6-5877)**	**20**	**2.48 (0.038-10.9)**
Freshwater fish	48	621 (97.8-2260)	8	1.29 (0.144-6.14)
Marine fish	24	999 (97.6-5877)	12	3.27 (0.038-10.9)
Seafood	**58**	**585 (49.1-4189)**	**10**	**0.457 (0.103-1.18)**
Crustacean	28	588 (154-2726)	4	0.606 (0.316-1.18)
Shellfish	14	358 (49.1-1660)	2	0.161 (0.118-0.205)
Cephalopod	16	776 (78.9-4189)	4	0.456 (0.103-0.813)
Dairy products	**58**	**261 (14.8-3020)**	**10**	**0.159 (0.087-0.256)**
Whole milk	38	53.3 (14.8-241)	10	0.159 (0.087-0.256)
Low-fat milk	5	149 (57.7-356)	-	-
Others	15	684 (16.4-3020)	-	-
Infant food	**40**	**404 (48.0-2223)**	**40**	**0.200 (0.028-2.90)**
Powdered formulas	15	439 (82.6-2196)	15	0.287 (0.028-2.90)
Rice Cereal	5	128 (48.0-222)	5	0.137 (0.088-0.268)
Malt extract	5	148 (83.6-278)	5	0.147 (0.090-0.239)
Biscuit	5	1132 (230-2223)	5	0.299 (0.231-0.376)
Puree	5	254 (51.6-848)	5	0.076 (0.057-0.093)
Supplementary (Essentials)	5	252 (85.3-571)	5	0.080 (0.074-0.087)

For samples with analytical concentrations less than the LOD, the LOD was used for the calculations.

Table 2. The 95th percentile of dietary exposures to PBDEs and Hexa-BBs in all age groups

Chemicals	0-3 yr old	4-6 yr old	7-12 yr old		13-16 yr old		17-18 yr old		19-65 yr old		> 65 yr old	
	All	All	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
BDE-47												
MCS P95	0.80	0.69	0.74	0.66	0.51	0.38	0.44	0.27	0.53	0.43	0.44	0.38
MOE	215	249	232	262	339	447	387	639	322	403	393	451
BDE-99												
MCS P95	0.52	0.52	0.64	0.58	0.51	0.40	0.47	0.29	0.39	0.28	0.24	0.19
MOE	8	8	7	7	8	11	9	14	11	15	18	22
BDE-153												
MCS P95	0.15	0.15	0.19	0.17	0.13	0.10	0.13	0.08	0.12	0.09	0.08	0.07
MOE	62	65	50	56	71	92	75	121	82	106	117	142
BDE-209												
MCS P95	17.57	11.60	10.99	10.42	8.19	6.61	7.54	4.87	6.91	5.89	6.46	5.70
MOE	96738	146522	154735	163084	207480	257018	225428	348850	246085	288591	263090	298171
ΣPBDEs												
EDI	9.38	8.51	7.05	6.53	5.79	4.48	5.18	3.35	4.79	4.06	4.34	3.65
MCS P95	21.52	15.43	15.02	13.49	10.93	8.73	9.87	6.53	9.54	7.98	8.48	7.60
ΣHxBBs												
MCS P95	0.019	0.012	0.012	0.010	0.008	0.006	0.007	0.005	0.008	0.007	0.007	0.006
NOEL	EFSA, 2010：NOEL=0.15 mg/kg bw/day (=150,000 ng/kg bw/day)											

MCS P95: the 95th percentile of estimated daily intake by Monte Carlo Simulation; Margins of exposure (MOEs)

EDI: estimated daily intake; Unit: ng/kg bw/day